Rheological Investigation of Entangled Hybrid Copolymers of Polystyrene (PS) with Polyhedral Oligosilsesquioxane (POSS)

Jian Wu[1], Timothy S. Haddad[2], Patrick T. Mather[1]*
[1]Dept. Chemical Engineering and [2]Polymer Program, University of Connecticut, Storrs, CT 06269
[2]ERC, Inc., AFRL/PRSM, Edwards Air Force Base, CA 93524

Abstract

The thermal properties and rheological behaviors of polystyrene (PS)-based thermoplastics bearing polyhedral oligosilsesquioxane (POSS) were investigated with variation of isobutyl (iBu)-POSS weight percentage. The incorporation of POSS-group significantly decreases the glass transition temperature and the rubbery plateau modulus. These findings are attributed to an influence of the nanometer-scale POSS pendant group on the microscopic topology of the host polymeric chains and negligible interactions between POSS and PS matrix.

Introduction

Because of their truly organic-inorganic hybrid chemical structure, Polyhedral oligosilsesquioxanes (POSS) have attracted more and more the attention of materials scientists and engineers interested in bridging the disparate property spaces occupied by polymers and ceramics. POSS features an inner silicon-oxygen (Si_8O_{12}) core functionalized at its silicon vertices with organic groups, one or more of which is chemically reactive, for example polymerizable. The incorporation of POSS molecules into polymeric materials by chemical reactions and/or physical blending can dramatically improve the physical properties, such as increasing the glass transition and oxidation resistance and the deceasing of heat evolution during combustion. Meanwhile, POSS molecules feature a well-defined nanoscopic size of 1~3 nm, a size comparable, upon limited aggregation, to the chain dimensions of typical polymeric hosts or backbones. Consequently, incorporating POSS comonomer along the backbone of a polymer chain can lead to dramatic changes the rheological behavior. Romo-Uribe [1] found that incorporation of POSS can decrease the zero shear viscosity of polystyrene, while Kopesky [2] found that POSS-tethered PMMA features a decrease of plateau modulus compared to the homopolymer.

In this paper, we report the thermal and rheological properties of a range of model POSS-containing polystyrene polymers in which the POSS wt-% was systematically varied.

Experimental Procedure

Random copolymers were synthesized from styrene and styryl-POSS with isobutyl R-group by radical co-polymerization in toluene at 60 °C (Figure 1). The product toluene solution was precipitated into an excess volume of n-hexane and filtered several times in order to remove unreacted monomers. The obtained products were then dissolved in THF and poured into casting dishes, where the solvent evaporated to form films. The cast films were then dried in a vacuum oven at 50-60 °C for two days and then 80-90 °C for an additional two days. Finally, trace THF was removed above the glass transition (T ~ 120 °C) for a half day further.

The thermal transitions of the samples were measured with a TA Instruments differential scanning calorimeter (Q-100 DSC) equipped with a mechanical intracooler (down to –60 °C) under a continuous nitrogen purge (50 mL/min). All measurements were conducted at a scan rate of 10 °C/min. The dynamic storage and loss moduli, $G'(\omega)$ and $G''(\omega)$, of the polymers were obtained from dynamic frequency sweeps using the ARES rheometer (Rheometric Scientific). All measurements were carried out within the linear viscoelastic range, which was confirmed by the lack of strain dependence of the dynamic storage modulus and loss modulus. Strain amplitudes were varied from 0.01 to 0.1, which was well within the linear viscoelastic regime of the materials investigated. The dynamic moduli were measured as a function of frequency, $0.01 < \omega < 100$ rad/s at various temperatures ranging from 120 to 180 °C for all of the samples investigated. The parallel plate geometry with plate diameters of 10 mm was used with sample thicknesses $0.5 < h < 1.0$ mm

Results and Discussion

The results of molecular characterization for random copolymers with iBuPOSS copolymerization loading ranging from 0 to 50wt% are detailed in Table 1. At 50 wt-% iBuPOSS, the mole fraction of POSS is only around 10 mol-%. As to copolymer randomness, it is well established that the chain microstructure has a close relationship with monomer reactivity ratios, r_i. If both r_1 and r_2 are close to 0, the copolymer will be alternating. When r_1 and r_2 are both close to 1, the product will be a

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14. ABSTRACT

The thermal properties and rheological behaviors of polystyrene (PS)-based thermoplastics bearing polyhedral oligosilsesquioxane (POSS) were investigated with variation of isobutyl (iBu)-POSS weight percentage. The incorporation of POSS-group significntly decreases the glass transition temperature and the rubbery plateau modulus. These findings are attributed to an influence of the nanometer-scale POSS pendant group on the microscopic topology of the host polymeric chains and negligible interactions between POSS and PS matrix.

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block copolymer. Finally, if r_1 and r_2 are close to 1 but each smaller than 1, the copolymer will random. Recently, Haddad *et al* [3] have determined the reactivity ratios of styryl iBuPOSS macromers with styrene in toluene reaction media, revealing $r_{styrene}$= 0.84 and $r_{styryl\text{-}iBuPOSS}$= 0.38. Thus, copolymers of styryl-iBuPOSS and styrene can reasonably be considered random. Although $r_{styrene}$ is larger than $r_{styryl\text{-}iBuPOSS}$, it is highly unlikely to generate blocky copolymers since iBuPOSS used in the present copolymerizations was held to less than 10 mol-% (~50 wt-%).

The effects of the presence of POSS cage on the glass transition were studied using differential scanning calorimetry (DSC) technique. The glass transition temperatures determined from the midpoint of enthalpy change at the second trace curve are shown in Figure 2. We find that the glass transition temperature of the random copolymers decreases with increasing iBuPOSS content. In other words, the iBuPOSS causes a plasticization of the PS main chain. In principle, the glass transitions of polymers reflect the rotation energy barrier about σ bonds in the backbone chain. The introduction of side chain or pendent group has two main effects on the glass transition. On one hand, the pendent group can restrict such torsional rotation about σ bonds in the backbone chain and increase the rotation energy barrier. On the other hand, the side group can increase the distance between adjacent backbone chains and thereby introduce additional free volume, effectively yielding and lower rotation energy barrier and a decrease in the glass transition temperature. Still further, if there were strong intermolecular interaction between pendent groups and/or between pendant group and polymer chain, the chain flexibility would decrease. Given the trend seen in Figure 2, it is apparent that increase free volume and the resulting decrease of rotation energy barrier bears a dominating effect in the present copolymers.

To examine the effect of iBuPOSS on the linear viscoelastic properties of PS random copolymers, complex modulus data were collected and time-temperature superposition applied, resulting in master curves. Frequency sweep data for a range of temperatures were shifted to a common reference temperature of 120 ^{o}C using both frequency shift factors (a_T) and modulus shift factors (b_T). The data in the master curves were ensured to be in the linear regime by obtaining the strain-independent viscoelastic properties as revealed by strain sweep tests.

The master curves of shear storage modulus, $G'(\omega)$ and shear loss tangent, tan δ= $G''(\omega)/G'(\omega)$, for various iBuPOSS wt-% are shown in Figure 3. The data extend over 7~8 decades in reduced frequency. Within the temperature range, time-temperature-superposition was found to be satisfactory and applicable as expected for linear homopolymers. Above glass transition temperature, there are three regimes observed from high frequency to lower one: glass-rubber transition regime, rubbery plateau regime due to chain entanglement and terminal zone regime due to chain. Within the rubbery plateau regime, the preferred method to estimate the plateau modulus would be to integrate the area under the terminal loss peak,

$$G_N^0 = \frac{4}{\pi} \int_{-\infty}^{\omega_{max}} G''(\omega) d\ln\omega \qquad (1)$$

where ω_{max} is the frequency at the maximum value of loss modulus G''_{max} in the plateau zone. However, since the samples prepared by radical co-polymerization are polydisperse, our data doesn't show terminal peaks in the loss modulus. Alternately, there are several semi-empirical ways to estimate the value of the rubbery plateau G_N^o. Wu[4] proposed an empirical relation for the relationship between the crossover modulus, G_c, [$G_c(\omega)$=$G'(\omega)$=$G''(\omega)$] and plateau modulus, G_N^o. The ratio of G_N^0 and G_c can be expressed as a function of molecular weight polydispersity, p=M_w/M_n,

$$\log\left(G_N^0 / G_c\right) = 0.380 + \frac{2.63(\log p)}{1 + 2.45(\log(p))} \qquad (2)$$

where p should be smaller than 3. This equation has been confirmed both theoretically and experimentally for many polymer systems. In addition, the plateau modulus can be determined by applying "tanδ minimum criterion": G_N^o is equal to the storage modulus G' at the frequency where tanδ is at its minimum in the plateau zone[4],

$$G_N^0 = \left|G'\right|_{\tan\delta\to min} \qquad (3)$$

Figure 4 shows the plateau modulus obtained from these two semi-empirical methods for our iBuPOSS random copolymers. In either case, the plateau modulus is monotonically decreasing with iBuPOSS content. The relationship between the characteristic value of G_N^o and critical molecular weight between entanglement points, M_e, is given by:

$$M_e = \frac{4}{5}\frac{\rho RT}{G_N^0} \qquad (4)$$

where R is the universal gas constant, ρ is density, and T is the absolute temperature. Based on Figure 4, the entanglement molecular weight of our PS copolymers apparently increases with increasing iBuPOSS loading. In this sense, the iBuPOSS groups pendant along the PS chain dilute entanglement density.

POSS molecules feature a well-defined 3-D structure with 1-3 nm scale size, comparable to the polymeric coil. From the viewpoint of chemical structure, POSS groups grafted on the PS chain may play a similar role of short branches, essentially altering the topology of the PS chain. Fetter *et al* [5] deal with the relationship between the entanglement density of polymer species and their

molecular dimensions in the melt state to find an empirical relation as following:

$$M_e = 218 \rho p^3 \qquad (5)$$

$$p = d_t / 19 \qquad (6)$$

where p is the packing length defined as the occupied volume of a chain divided by the mean square end-to-end distance and d_t is the tube diameter, which is related to the chain profile. Combining these two equations and Eqn. (4), we can obtain the relationship between critical entanglement molecular weight, plateau modulus, and tube diameter.

$$M_e = 0.03178 \rho d_t^3 \qquad (7)$$

$$G_N^0 = \frac{0.00494 k_B T}{d_t} \qquad (8)$$

Such empiricism has been confirmed by simulations.[6] Equation (8) reveals that the plateau modulus is inversely proportional to tube diameter: $G_N^0 \sim d_t^{-1}$. From the topological viewpoint, we can reasonably explain the relation between plateau modulus and iBuPOSS content observed. Undoubtedly, the pendant iBuPOSS has a great influence on the PS chain topology. If the dynamics of the random copolymers follows tube model theory, the resultant average tube diameter will increase due to the presence of the pendent iBuPOSS molecules. Consequently, the plateau modulus should monotonically decrease with POSS content due to variation in microscopic topology of the PS main chain.

Considering the terminal zone, a homopolymer usually behaves like an ideal Newtonian fluid with viscosity being independent of shear frequency or rate. The expected frequency dependence of storage and loss moduli in the terminal zone is as follows: $G'\sim\omega^2$ and $G''\sim\omega^1$. Here, the terminal slope of G' shown in Figure 3 features deviation (smaller values) from 2. Such behavior might indicate persistence of a loose network of physical intermolecular interactions; however, we observe only monotonic increase in tanδ with decreasing frequency – no maximum that would implicate relaxation of such intermolecular interactions. Therefore we ascribe the observed deviation of the G' slopes from 2 to molecular weight polydispersity and that intermolecular interactions between iBuPOSS and PS matrix do not play an essential role in determining rheological behavior. Such a conclusion contrasts with our earlier work[1] on PS-POSS copolymers featuring cyclohexyl, rather than isobutyl, corner groups on POSS.

Summary

Here, we reported the thermal and linear rheological behavior of random copolymers from styrene and styryl-based iBuPOSS. The iBuPOSS plays a plasticizer role and makes the glass transition temperature decrease with increasing POSS content. Rheological measurements showed that the linear viscoelastic properties of the random copolymers follows time-temperature-superposition principle well over a range of iBuPOSS contents up to 50 wt-%. We observe that rubbery plateau modulus to monotonically decrease with iBuPOSS loading. We postulate that the introduction of iBuPOSS influences chain topology, diluting the entanglement density and, thereby, decreasing the plateau modulus.

Acknowledgements

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Key Words

POSS, Polystyrene(PS), Glass transition, Rheology.

Table 1. Molecular Characterization of Random Copolymers of Styrene and Styryl-iBuPOSS

Compound	M_w (kg/mol)*	M_w/M_n*	DP*	wt-% POSS[#]	mol-% POSS[#]
0wt%iBuPOSS	161	1.43	1080	0	0
6wt%iBuPOSS	186	1.46	1164	5.9	0.70
15wt%iBuPOSS	195	1.40	1158	15.4	2.02
30wt%iBuPOSS	300	1.52	1387	33.2	5.34
50wt%iBuPOSS	419	1.65	1358	52.1	10.95

*:Molecular weight data was obtained from GPC (in $CHCl_3$);
#:Weight and molar percentage were obtained from ^{1}H-NMR (in $CHCl_3$).
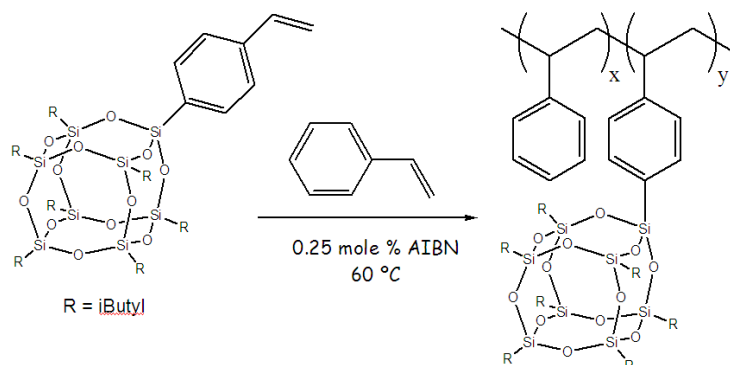
Figure 1. Synthetic scheme for the preparation of random copolymers obtained from styrene and styryl isobutyl-POSS (iBuPOSS) through radical co-polymerization initiated by AIBN at 60 ^{o}C.
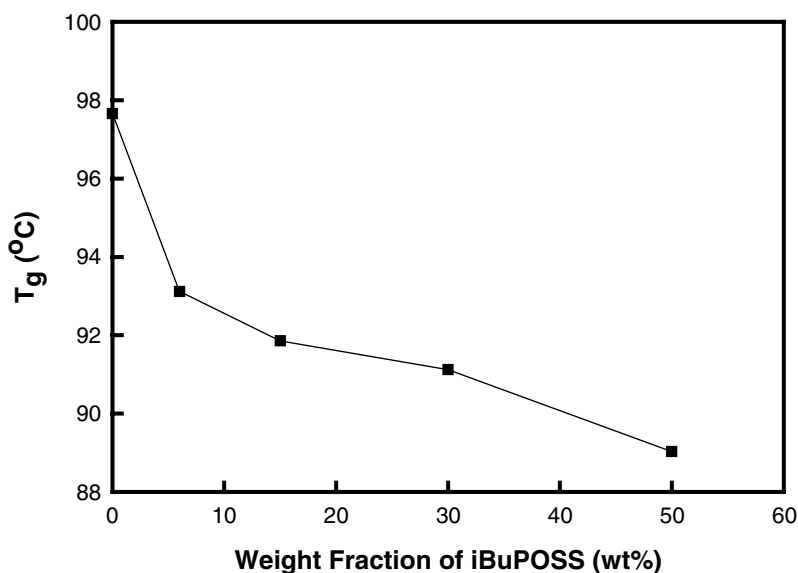

Figure 2. The glass transition temperatures (T_g) for as-cast iBuPOSS-PS copolymers films as the function of iBuPOSS content. T_g was determined from the midpoint of enthalpy change in the second Differential Scanning Calorimetry (DSC) trace curves with ramping rate of 10 ^{o}C/min.
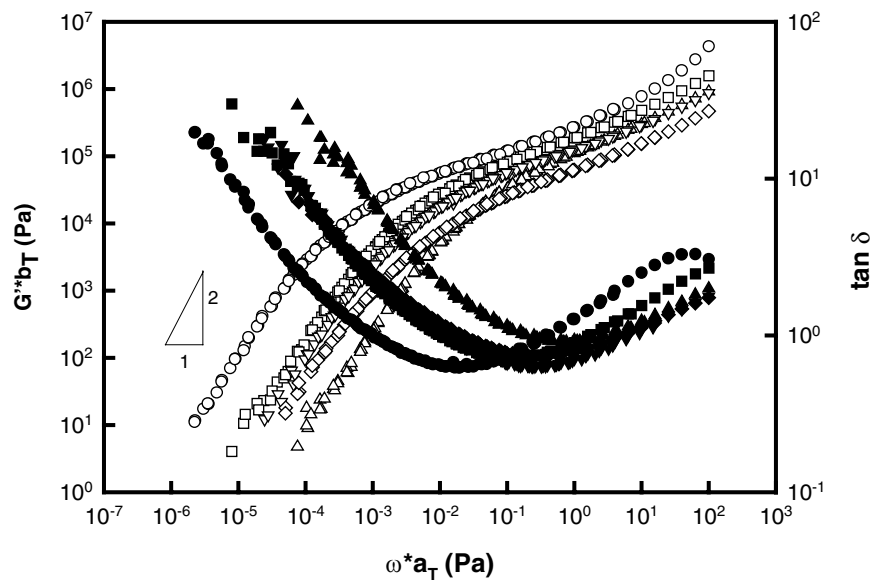
Figure 3. Master Curve of G′ (open symbols) and tan δ (filled symbols) for as-cast films of iBuPOSS-PS copolymers with varying weight percentage of iBuPOSS: (○) 0, (□) 6, (△) 15, (▽) 30, and (◇) 50 wt-% POSS with reference temperature 120 °C.
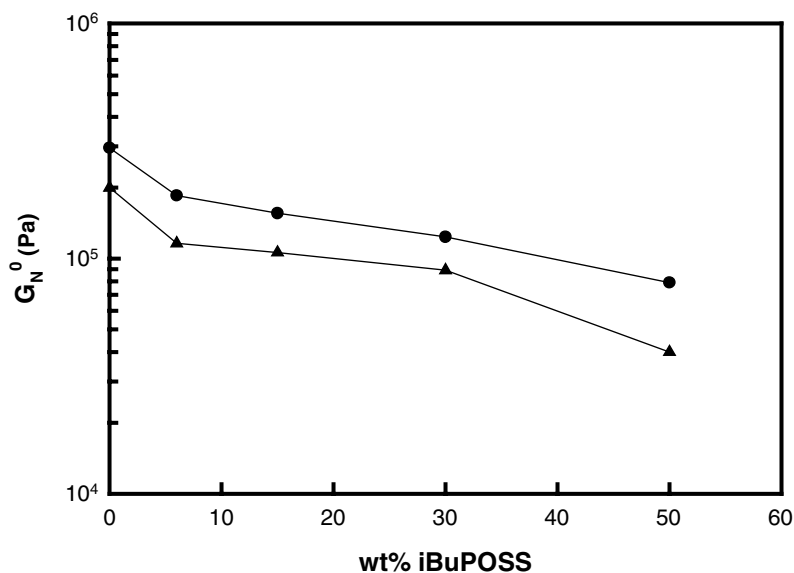

Figure 4. Rubbery Plateau Modulus (G_N^o) of as-cast films of iBuPOSS-PS copolymers with varying weight percentage of iBuPOSS as a function of POSS weight fraction. G_N^o is determined by two semi-empirical ways: (●) evaluated from the crossover modulus and molecular weight polydispersity and (▲) determined from G′ at minimum tanδ.